CRYSTAL CHEMICAL AND QUANTUM CHEMICAL STUDIES OF Ba(Sr)-Nb OXIDE COMPOUNDS

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The information available on the BaO(SrO)-NbO-NbO_2 system with the niobium atom in the lower oxidation degree is very limited. Very few compounds have been found previously in this system. They are $BaNbO_3$, Sr_xNbO_3(0,7≤x≤1), $Ba_2Nb_2O_9$, $SrNb_8O_{14}$ and some suggestions on the $BaNb_8O_{14}$ existence have been made also. At the same time Nb-based oxide compounds could be quite interesting in the search of new noncopper high T_c superconductors (see, for example, [1,2]).

In the present paper we have studied Ba(Sr)-Nb_xO_{2x-2} (I) and $Ba_2(Sr_2)$-Nb_xO_{2x-1} (II) compositions in the phase diagram of BaO(SrO)-NbO-NbO_2 system. The synthesis of the materials has been carried out in vacuum at the temperatures of 1000-1500 C. Barium carbonate and niobium pentoxide have been used as initial components. X-ray analysis has been carried out at DRON-UM1 CuK_α radiation.

In the subsystem (I) the following individual compounds have been obtained: $BaNb_4O_6$ (x=4), $BaNb_5O_8$ and $SrNb_5O_8$ (x=5), $BaNb_8O_{14}$ and $SrNb_8O_{14}$ (x=8). In the subsystem (II) $Ba_2Nb_5O_9$ and $Sr_2Nb_5O_9$ (x=5) have been separated only. The crystal structure of the compounds obtained has been studied dy the neutron difraction experiments with the use of Rietveld analysis. The crystal lattice of $BaNb_4O_6$, $Ba_2Nb_5O_9$ and $Sr_2Nb_5O_9$ appears to have P4mmm, z=1 space group and they represent the series of n·($BaNbO_3$)·3(NbO) compounds with $a_T \approx a(NbO)$, $c_T \approx (n+1)\cdot a(BaNbO_3)$, where n is the thickness of perovskite layer. All of the compounds obtained have typical perovskite layered structure with two-dimensional perovskite layers and niobium monoxide layers perpendicular to c axis. $BaNb_5O_8$ contians one-dimentional cluster of niobium monoxide, which is parallel to c axis. This compound possesses the P4/m, z=1 space group lattice. Crystal lattice parameters are closely related with niobium monoxide block size: a_T=6,608A ≈ $\sqrt{5/2}$ a(NbO), c_T=4,107A≈ ≈ a(NbO). $BaNb_8O_{14}$ and $SrNb_8O_{14}$ are isostructural (of Pbam, z=2 space group) and contain chains of isolated niobium monoxide clus-

ters.

The study of electrophysical properties carried out reveals the compounds with one-dimentionalniobium monoxide clusters - $BaNb_5O_8$ and two-dimentionalclusters - $BaNb_4O_6$, $Ba_2Nb_5O_9$, $Sr_2Nb_5O_9$ are paramagnetics of the Curie-Weiss type and reveal the metallic character of $\rho(T)$ dependence ($\rho_{293} \approx 10^{-4}$ om·cm). At the same time the compounds with isolated clusters - $BaNb_8O_{14}$ and $SrNb_8O_{14}$ are weak diamagnetics at the room temperature and have metal-semiconductor phase transition at $T_t \approx 270K$. Isomorphic substitution of Ba(Sr) for La results in the shift of phase transition to the low temperature region (1% of La - $T_t \approx 80K$, 2% of La - $T_t \approx 10K$).

The next peculiarity of $BaNb_8O_{14}$ and $SrNb_8O_{14}$ compounds is their tendency to oxygen absoprtion, their mass is increased by 1% under the yeat treatment (T=250 C) in the air.

The results obtained show that all the Sr and Ba niobium oxides with the niobium in the lower oxydation states form the lattices containing niobium monoxide clusters which could be isolated, one- or two-dimentional. Compound with isolated clusters satisfay the superconductivity criterion by Sleight [3]. The metal-semiconductor phase transition appear to realize at electron concentration in the clusters equal to 14 instead of 22 as in Shevrel phases.

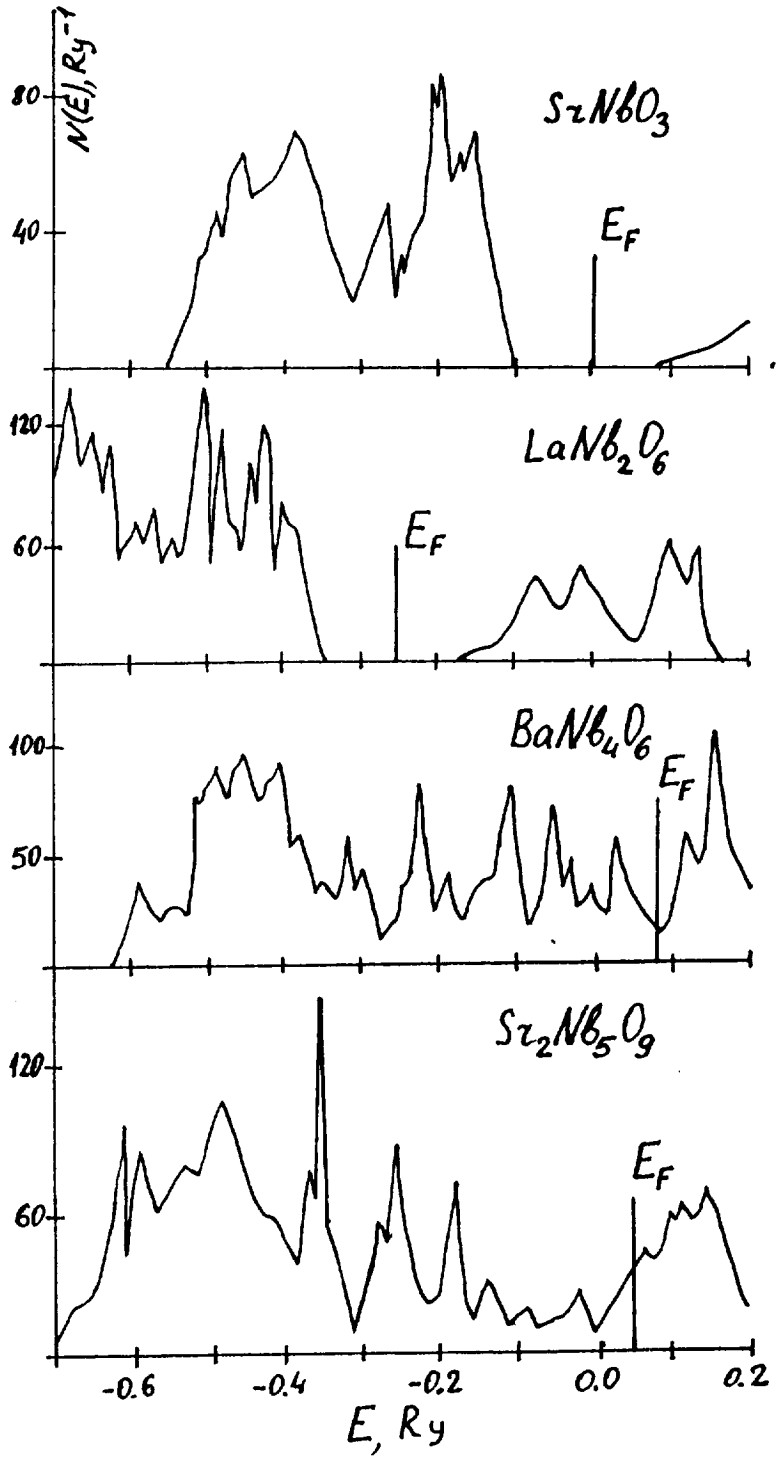

Fig. 1. The total density of states

In order to estimate of some of the compounds obtained possess similar pecualiriti es in electronic structure as copper high-T_c superconductors, we carried out the LMTO band structure calculations for the following niobium compounds: $SrNbO_3$, $La_{0,66}Nb_2O_6$,

$BaNb_4O_6$, $Sr_2Nb_5O_9$. The calculations performed showed that for the $SrNbO_3$ and $La_{0,66}Nb_2O_6$ compounds Nb4d and O2p bands are completely separated and the Fermi level is situated between them.

In the $BaNb_4O_6$ and $Sr_2Nb_5O_9$ partial hibridization of Nb4d and O2p states at the energies lower then E_F takes place and the common Nb4d-O2p band is formed (Fig.1). For $BaNb_4O_6$ O2p contributions at the Fermi energy (which are typical for high-T_c copper superconductors) are missing, but for $Sr_2Nb_5O_9$ quite essential oxygen atoms contributions at the E_F appear. Their value could be significantly increased when the Fermi level is shifted, for example, when doping the crystal lattice by atoms of another valence or changing the oxygen stehiometry ratio. In some cases, probably, the characteristic picture of high-T_c superconductor electronic structure could appear together, hopefully, with superconductivity properties.

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